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Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 4

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16. ABSTRACT

EPA established drinking water regulations for ten inorganic substances and radionuclides that became effective on June 24, 1977. As a result of these new regulations, many communities may be required to construct new treatment facilities or to modify existing ones. This paper (Part 4) on chromium and mercury reviews existing treatment technology for meeting the EPA drinking water regulations. The effectiveness of conventional coagulation, lime softening, ion exchange, activated carbon, reverse osmosis, and electrodialysis for the removal of the two contaminants are discussed. The information consists of the results of DWRD recent laboratory and pilot plant studies and information from a general literature review.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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of a representative sample for quality assurance testing.

Further investigation is also necessary to determine whether this fractionation occurring in chlorine cylinders will result in periods of higher carbon tetrachloride contamination at small water utilities that use the same cylinder of chlorine over a long period of time.

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A section paper selected by the JOURNAL, authored by Patrick R. Cairo (Active Member, AWWA), chief, res. and dev. div., and Bruce S. Aptowicz (Active Member, AWWA), chief, treatment sect., both of the Philadelphia Water Dept.; and Ramon G. Lee (Active Member, AWWA), chief, and William M. Blankenship, tech. advisor, both of the water supply branch, USEPA Region 3, Philadelphia, Pa.

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Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Organics: Part 4

Thomas J. Sorg

The fourth in a series summarizing existing treatment technology to meet the inorganic National Interim Primary Drinking Water Regulations, this report describes current treatment methods for removing chromium and mercury from drinking water.

Chromium Removal From Water

Health effects. Chromium first appeared in the USPHS Drinking Water Standards[1] in 1946 because several studies showed that chromium readily induced skin sensitizations, and the hexavalent form produced lung tumors when inhaled.[2-4] The limit established as grounds for rejection of a water supply was 0.05 mg/L (as hexavalent chromium), the lowest amount analytically determinable at the time. For the same health reasons chromium was maintained in the 1962 PHS Standards[5] and the 1975 EPA National Interim Primary Drinking Water Regulations (NIPDWR).[6] EPA introduced one slight change in the regulation by extending the limit to total chromium rather than for only the hexavalent form. Although the trivalent form is not considered toxic, EPA made the change because the normal analytical detection method (atomic adsorption spectrophotometry) does not distinguish between the valence states and because the hexavalent form is the one most likely to be found in drinking water.

Chromium has not been proved to be either an essential or a beneficial element, but some studies suggest that microgram amounts of the trivalent form derived primarily from food are essential for maintenance of normal glucose metabolism.[7] Moreover, the National Academy of Science (NAS) states that some animal studies indicate that chromium deficiency may induce arteriosclerosis. Because diets containing most processed foods may be chromium deficient and because tissue chromium in US adults has been shown to decline with age, the NAS suggests that chromium deficiency may be a greater problem than chromium in drinking water.

Although hexavalent chromium is known to produce lung tumors when inhaled, the amount of chromium that can be ingested over a lifetime without producing adverse health effects is still virtually undetermined. MacKenzie et al[8] studied the toxicity to rats of chromate (Cr VI) and chromic (Cr III) ion at various levels in drinking water. No toxic effects were observed in the rats when drinking water containing 0.45-25 mg/L of either form was ingested for a year. Significant accumulation of chromium in tissues occured at concentrations above 5 mg/L. More recent studies with dogs showed no effects with 11 mg/L of hexavalent chromium over four years.[9] Higher doses, however, produced erosion of the gastrointestinal tract and kidney lesions.

The maximum contaminant level

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with the Chlorine Institute and representative chlorine manufacturers to establish an interim maximum level for carbon tetrachloride content in chlorine used for water treatment. This interim level was established at 100 mg/L by EPA and agreed to by the manufacturers' association, pending an assessment of what the chlorine industry is currently producing and what it is capable of producing with available technology.

Summary and Recommendations

Abnormally high levels of carbon tetrachloride were first detected in Philadelphia drinking water during routine monitoring of volatile halogenated organics by the Philadelphia Water Department. After an intensive investigation of both the raw water supply and the various plant unit processes, this chemical was found to be a contaminant in the chlorine used by the city. The regional office of EPA further discovered that more than 100 other water utilities being served by the same chlorine manufacturer were experiencing similar levels of carbon tetrachloride. The problem was quickly resolved by an immediate transfer to other sources of chlorine while the manufacturer rectified its chemical process to reduce the level of organic contaminants. The result of this incident has been the establishment by EPA of an interim maximum level of 100 mg/L carbon tetrachloride in chlorine and the requirement of improved quality control on the part of all chlorine manufacturers.

The incident has demonstrated the need for establishing more rigorous quality standards for chlorine. The AWWA standard for liquid chlorine specifies that "chlorine shall be 99.5 percent pure by volume as obtained from vaporized liquid chlorine . . ."[1] It further specifies that the chlorine be "suitable for the treatment of water, sewage and industrial wastes." This standard, approved in 1959, adequately reflected then-current drinking water standards and objectives and ensured safety in the delivery and application of chlorine. However, more recent awareness of potential human health problems associated with exposure to low level organic compounds and the concomitant advances in routine laboratory techniques for their monitoring demand that new safeguards be implemented in the manufacture of all chemicals used in the treatment of drinking water.

In the case of chlorine the problem of ensuring its quality is further aggravated by difficulties involved in testing the chemical. The differing volatilities of chlorine and the organic contaminants of concern result in fractionation in the container vessel or sample cylinder. Further analytical work is needed to develop a method ensuring the collection

TABLE 3
Samples Collected by EPA During Period of Contaminated Chlorine Use

Finished Water Sampling Location	Contaminated Supply Date	Contaminated Supply CCl_4 Concentration* µg/L	Alternate Supply Date	Alternate Supply CCl_4 Concentration* µg/L
Philadelphia, Pa.				
Belmont Plant	11/14	10.2	11/21	<0.1
	11/15	9.2†		
	11/17	30.0		
Queen Lane Plant	11/14	6.3	11/21	<0.1
	11/15	2.8		
	11/17	16.8		
Norristown, Pa.	11/15	13.5†		
	11/17	11.0		
Philadelphia Suburban Water Co.				
Neshaminy Plant	11/17	8.7	12/6	<0.1
	11/21	33.0		
Crum Creek Plant			12/6	<0.1
Wilmington Suburban Water Co.	11/17	0.4	1/12/78	trace
	12/6	4.5		
Kennett Square, Pa.	12/6	12.0	1/12/78	<0.1
Media, Pa.			12/6/78	<0.1
New Castle, Del.			1/16/78	<0.1
Smyrna, Del.			1/16/78	<0.1
Newark, Del.			1/16/78	<0.1
Elkton, Md.			1/12/78	<0.1
Cambridge, Md.			12/07/77	<0.1
Easton, Md.			12/07/77	<0.1
St. Michaels, Md.			12/07/77	<0.1
Rock Hall, Md.			12/02/77	<0.1

*Analyzed by purge-and-trap procedure.
†Confirmed by GC-MS.

TABLE 4
Systems Using Chlorine Produced and Supplied Before CCl_4 Contamination

Finished Water Sampling Location	Date	CCl_4 Concentration– µg/L
Newport, Del.	1/16/78	0.17
Quakertown, Pa.	1/11/78	<0.1
Lehigh City, Pa.	1/11/78	trace
Hellertown, Pa.	1/11/78	<0.1
Uwehlan, Pa.	1/11/78	<0.1
Downingtown, Pa.	1/11/78	trace

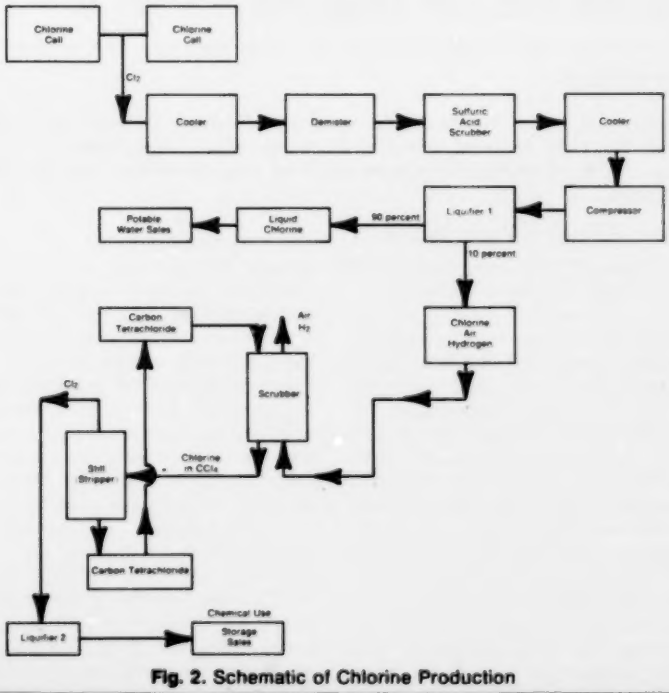

Fig. 2. Schematic of Chlorine Production

(MCL) of 0.05 mg/L is one hundredth of the maximum concentration having no observed adverse effect on health.[7] This level is also the limit established by the World Health Organization (WHO) and by the Japanese, although these two limits are set in terms of hexavalent chromium only. The NAS recommended studies to further define the carcinogenic potential of ingesting both chromium forms.[7] The academy also suggested the return to the WHO limit for chromium VI only, if a suitable analytical technique could be developed to distinguish between the two forms.

Chromium is not expected to pose a serious problem for the water utility industry because it is not commonly found in either ground or surface drinking waters. Kropp and Kroner[10] reported only 24.5 percent of 1577 water samples from rivers and lakes contained detectable amounts of chromium. The range of sample values was 0.001 to 0.112 mg/L and the mean was 0.0097 mg/L. Durum et al[11] also reported low concentrations in US surface waters. Chromium was found in only eleven of 700 samples and no concentrations were above 0.05 mg/L.

The 1969 Community Water Supply Study[12] showed only four finished water samples from 967 water supplies (less than one percent) with total chromium concentrations above 0.05 mg/L. The maximum level found, 0.097 mg/L, was only slightly above the MCL. A very recent cardiovascular disease study attempting to develop relationships between inorganics in tap water and cardiovascular mortality rates also showed low incidences of chromium in finished drinking water.[13] Tap water samples from 3834 households and 1400 water plants in 35 geographical areas in the US showed 28 percent had chromium concentrations above the detection limit of 0.0001 mg/L. The concentrations ranged from 0.00043 to 0.008 mg/L and the mean value was 0.00179 mg/L, further indicating the lack of a serious chromium problem for the water utility industry. Because the principal source of chromium in natural waters is industrial discharge from the metal finishing, textile, and leather industries, the greatest potential for a chromium problem exists with water sources containing discharges from these industries.

Chromium chemistry overview. Chromium has several oxidation states, but only the trivalent and hexavalent ones are significant in aqueous systems. Trivalent chromium occurs as a cation and the hydroxide complex is very insoluble. Hexavalent chromium occurs as an anion as either chromate ($HCrO_4^-$ / CrO_4^{-2}) or dichromate ($Cr_2O_7^{-2}$). Both anion forms are very soluble and the formation of each is pH dependent. The chromate ion exists in alkaline water and can be readily converted to the dichromate ion by acidifying the solution. The reaction is reversible; the addition of hydroxyl ions changes the dichromate to the chromate ion. Dichromates in acid solutions are strong oxidizing agents and thus are capable of being reduced to the chromic ion. This principle is commonly used in treating industrial wastewater for the removal of chromates and dichromates; both anion forms are converted to chromium III and precipitated out as chromium hydroxide ($Cr(OH)_3$).

Because chromium ores are not common to the US, the principal source of chromium in natural waters is industrial discharge to surface waters. Chromium in industrial wastes is predominantly chromate and dichromate, and therefore chromium VI should be the primary form found in surface waters. The trivalent form may also occur, however. Some industries employ this form directly in the manufacturing process, and waste treatment practices normally convert chromium VI forms to chromium III for removal.

Because chromium hydroxide is very insoluble and adsorbed much more readily to naturally occurring solids than the chromium VI, the oxidation and reduction characteristics of natural water will greatly influence the distribution of chromium in water. Schroeder and Lee[14] studied the oxidation of chromium III and the reduction of chromium VI in natural waters. The authors indicate that, in theory, at pH 6.5 to 8.5 and under oxygenated natural water conditions, chromium VI is the thermodynamically stable species. Under the same conditions, chromium III could also be kinetically stable. Experiments to determine the oxidation of chromium III by oxygen showed that the oxidation rate is slow in natural waters and that other reactions, such as adsorption, may occur before chromium III can be oxidized. Temperature was also significant; at room temperature, 22-26°C, about 3 percent of the chromium III was oxidized in 30 days, and at 45°C the same amount of oxidation occurred in less than three days. Studies on the effect of pH showed the rate of oxidation not to be affected over the pH range of 5.9 to 9.9.

The reduction of 0.1 mg/L chromium VI with varying concentrations of ferrous iron (0.4-1.2 mg/L) at pH 7.1, 7.5, and 9.1 was studied.[14] Laboratory experiments revealed that ferrous iron will reduce chromium VI, but the extent of reduction is dependent on pH, the concentration of ferrous iron, and the degree of oxidation of the ferrous iron by the oxygen in the water. A ferrous iron concentration of 0.4 mg/L achieved 73 percent reduction of chromium VI to III at pH 9.1; approximately one half of the original ferrous iron was oxidized by chromium VI and half by oxygen. At an initial pH of 9.1, the ferrous iron-oxygen reaction was favored, and thus on[illegible] percent of the chromium VI [illegible] reduced. When 1.2 mg/L of ferrous i[illegible] were utilized at pH 7.1, almost 1[illegible] percent of the chromium VI was reduce[illegible] to chromium III.

The reducing effect of sulfides and natural organics on chromium VI was also investigated by Schroeder and Lee.[14] Test results indicated that dissolved sulfides can rapidly reduce chromium VI and that natural organics have litte effect.

The solubility of most pure metal hydroxides is a function of pH, and chromium hydroxide is no exception. Nilsson[15] showed that the solubility of chromium hydroxides decreases as the pH increases from about pH 5 to 8. If the pH is increased with sodium hydroxide, the solubility of the hydroxide complex will rise when the pH goes above 8. If the pH rise is brought about with lime, the chromium solubility does not rise because the solubility of calcium chromite is also relatively low. Parsons[16] also showed that the lowest solubility range for chromium III is 8.5 to 9.5 when lime is used to adjust pH.

Thomas and Theis[17] studied the effects of selected ions on the removal of chromium hydroxide from industrial wastewater and also found the removal of chromium hydroxide to decrease above pH 8 when sodium hydroxide was used for pH adjustment. When lime was used to adjust pH, good chromium III removal was achieved from pH 7 to 11.5. The calcium ion from the use of lime for pH adjustment is beneficial both in removing CO_3^{-2} from solution and in acting as a doubly charged counterion to the negatively charged colloid, $Cr(OH)_3$, present at high pH. These same authors indicated that the carbonate and phosphate ions hinder chromium III removal. The literature on the behavior of chromium as applied to water supply treatment can be summarized as follows:

1. Both trivalent and hexavalent chromium may exist in natural water, but the hexavalent is the form more likely to be found because chromate and dichromates are very soluble. Besides being very insoluble, chromium III is easily adsorbed onto natural solids.
2. Hexavalent chromium cannot be removed by conventional water treatment methods unless it is converted to the insoluble trivalent form.
3. Ferrous iron and sulfides are capable reducing agents for converting chromium VI to III. Low pH provides the best environment for reduction.
4. The solubility of trivalent chromium decreases slightly with pH; the ideal range for removal is pH 8-10. If pH adjustment of the water is required, lime will provide higher removal than that provided by sodium hydroxide.

Treatment methods. Because chromium

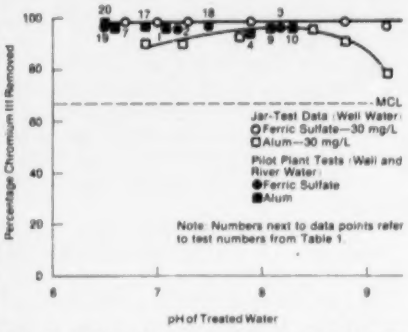
Percentage Chromium III Removed
pH of Treated Water
MCL
Jar-Test Data (Well Water)
Ferric Sulfate—30 mg/L
Alum—30 mg/L
Pilot Plant Tests (Well and River Water)
Ferric Sulfate
Alum
Note: Numbers next to data points refer to test numbers from Table 1.

Fig. 1. Effect of pH on Chromium III (0.15 mg/L) Removal by Coagulation Treatment

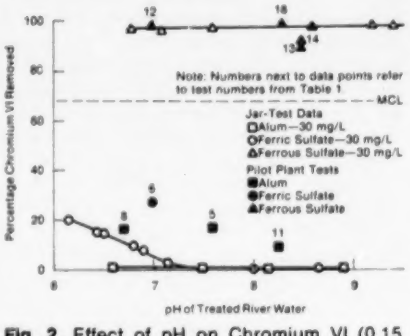

Fig. 2. Effect of pH on Chromium VI (0.15 mg/L) Removal by Coagulation Treatment

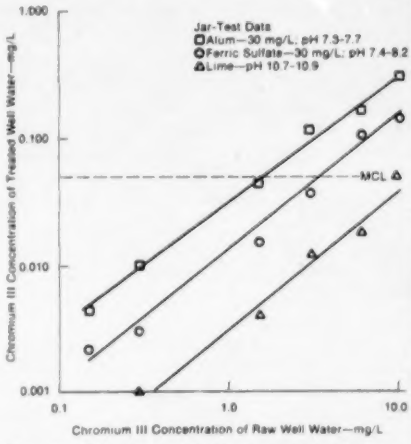
Jar-Test Data
Alum—30 mg/L; pH 7.3-7.7
Ferric Sulfate—30 mg/L; pH 7.4-8.2
Lime—pH 10.7-10.9
MCL
Chromium III Concentration of Treated Well Water—mg/L
Chromium III Concentration of Raw Well Water—mg/L

Fig. 3. Effect of Initial Concentration on Chromium III Removal by Coagulation and by Lime Softening Treatment

TABLE 1

Results of Conventional Coagulation Pilot Plant Tests for Chromium Removal

Test Number	Date Started	Length of Test hr	Test Water*	Coagulant Type	Coagulant Dose mg/L	pH of Treated Water	Chromium Contaminant Form	Chromium Contaminant Average Raw Water Concentration mg/L	Percentage Chromium Removed Settled Water	Filtered Water Dual Media Filter	Filtered Water Granular Activated Carbon Filters Virgin GAC†	Filtered Water Granular Activated Carbon Filters Exhausted GAC†	Filtered Water Granular Activated Carbon Filters Virgin GAC‡
1	10/4/76	92	Ohio River	alum	34	7.1	Cr III	0.12	>96	>96	>96	>96	–
2	10/18/76	93	Ohio River	ferric sulfate	28	7.2	Cr III	0.12	84	>96	>96	>96	–
3	11/1/76	106	Ohio River	ferric sulfate	28	8.2	Cr III	0.13	90	>96	>96	>96	–
4	11/8/76	102	Ohio River	alum	30	7.9	Cr III	0.13	81	>94	>94	>94	–
5	11/15/76	108	Ohio River	alum	30	7.6	Cr VI	0.13	8	17	30	22	–
6	1/24/77	72	Ohio River	ferric sulfate	24	7.0	Cr VI	0.14	15	27	24	10	–
7	4/11/77	100	Ohio River	alum	31	6.6	Cr III	0.14	92	>96	–	>96	>96
8	4/18/77	100	Ohio River	alum	32	6.7	Cr VI	0.14	11	16	–	13	35
9	5/2/77	100	Ohio River	alum	29	8.1	Cr III	0.14	73	>96	–	>96	>96
10	6/13/77	100	Ohio River	alum	29	8.3	Cr III	0.12	69	>96	–	>96	>96
11	6/20/77	100	Ohio River	alum	30	8.2	Cr VI	0.45	7	9	–	9	11
12	8/8/77	89	Ohio River	ferrous sulfate	33	7.0	Cr VI	0.16	55	>97	–	>97	>97
13	8/15/77	93	Ohio River	ferrous sulfate	28	8.5	Cr VI	0.13	73	89	–	89	88
14	8/22/77	91	Ohio River	ferrous sulfate	29	8.5	Cr VI	0.12	76	91	–	93	93
15	8/29/77	90	Ohio River	ferrous sulfate	30	8.6	Cr VI	1.20	71	79	–	78	79
16	9/19/77	72	Ohio River	ferrous sulfate	32	8.3	Cr VI	0.31	78	>98	–	>98	>98
17	1/23/78	58	well water	alum	27	6.9	Cr III	0.15	77	>97	–	>97	>97
18	2/6/78	70	well water	ferric sulfate	33	7.5	Cr III	0.14	67	>97	–	>97	>97
19	2/13/78	90	well water	ferric sulfate	30	6.5	Cr III	0.15	83	>97	–	>97	>97
20	2/27/78	90	well water	alum	30	6.5	Cr III	0.21	49	>98	–	>98	>96

*Water spiked with either $CrCl_3$ (Cr III) or $Na_2Cr_2O_7$ (Cr VI).
†Filtrasorb 300, Calgon Corp., Pittsburgh, Pa.
‡Hydrodarco 1030, ICI Americas, Inc., Wilmington, Del.

is utilized either directly or indirectly in many manufacturing processes, treatment techniques to remove or recover chromium from industrial wastewaters have been well developed and documented. Information also exists on chromium removal from municipal wastewater. For the treatment of drinking water, however, few studies have been reported because chromium has not been a serious problem.

The Drinking Water Research Division (DWRD), USEPA, at the Environmental Research Center in Cincinnati, Ohio, conducted laboratory and pilot plant studies for chromium removal by conventional coagulation and lime softening methods. Detailed information on the results of these studies follows. Limited information is also available on treatment by ion exchange, activated carbon adsorption, and reverse osmosis.

Conventional coagulation. DWRD ran laboratory jar tests and pilot plant studies to evaluate the effects of several operating parameters on the removal of chromium III and VI from surface and groundwaters by coagulation treatment. Although solubility data for chromium hydroxide indicates a pH dependency (with the lowest solubility at pH 8-9), jar-test experiments with chromium-III-spiked well water showed no pH effect for ferric sulfate removal, and only a slight effect with alum removal (Fig. 1). Ferric sulfate removals were near 100 percent from pH 6.5 to 9.5. Alum was less effective and achieved best results of around 90 percent removal between pH 7.5 and 8.5. Above and below this pH range, removals were slightly lower at 80-90 percent.

The literature indicates that chromium VI is not removed by alum and ferric sulfate coagulation because the chromate and dichromate ions are very soluble, and DWRD jar-test studies confirmed this (Fig. 2). Essentially no chromium VI removal was achieved by either alum coagulation from pH 6.5 to 9 or by ferric sulfate from pH 7.5 to 9. Below pH 7.5, ferric sulfate removals increased with decreasing pH, but the maximum achieved was only about 20 percent at

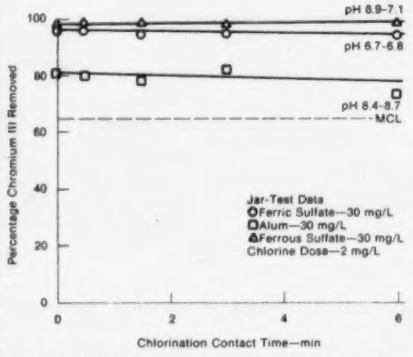

Fig. 4. Effect of Prechlorination Contact Time on Chromium III (0.15 mg/L) Removal From River Water by Coagulation Treatment

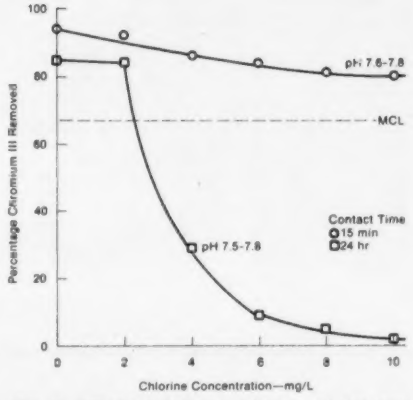

Fig. 5. Effect of Chlorine Dose and Contact Time on Chromium III (0.15 mg/L) Removal From Well Water by Alum Coagulation

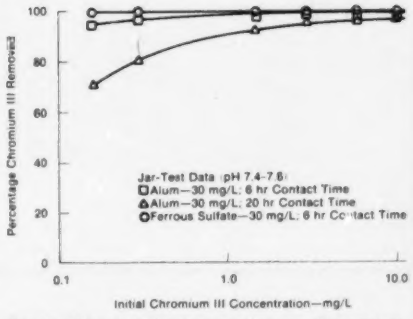
Jar-Test Data (pH 7.4-7.6)
Alum—30 mg/L; 6 hr Contact Time
Alum—30 mg/L; 20 hr Contact Time
Ferrous Sulfate—30 mg/L; 6 hr Contact Time
Percentage Chromium III Removed
Initial Chromium III Concentration—mg/L

Fig. 6. Effect of Prechlorination on Chromium III Removal From Well Water by Coagulation Treatment

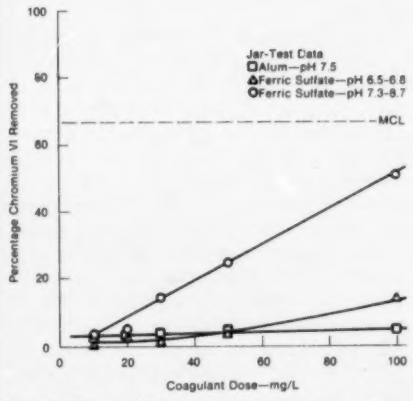

Fig. 7. Effect of Coagulant Dose on Chromium VI (0.15 mg/L) Removal

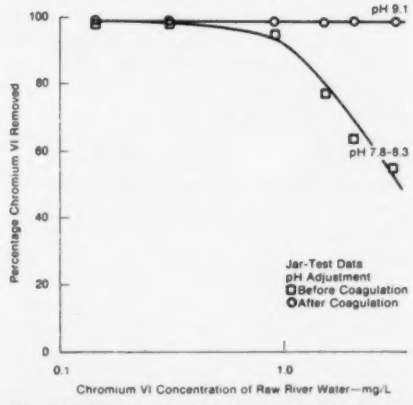

Fig. 8. Effect of pH Adjustment on Chromium VI (30 mg/L) Removal by Ferrous Sulfate Coagulation

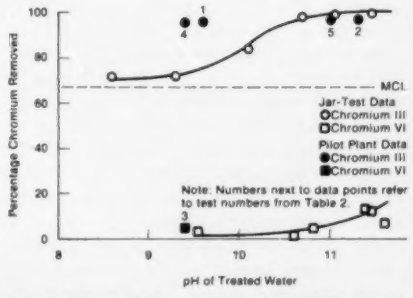

Fig. 9. Effect of pH on Chromium (0.15 mg/L) From Well Water by Lime Softening

pH 6. When ferrous sulfate, a coagulant sometimes used for chromium VI removal from industrial wastewater, was tried, excellent removals of 95 percent and greater were obtained from pH 6.5 to 9.5. These test results indicate that ferrous sulfate is capable of reducing chromium VI to III as the ferrous ion oxidizes to the ferric ion.

Pilot plant tests on removing chromium III and VI by conventional coagulation treatment were conducted with the pilot plant system and procedures described in Part 2.* The test waters were Ohio River water and Glendale, Ohio, well water. Because neither test water contained naturally occurring chromium, both were spiked with chromium chloride (Cr III) or sodium dichromate (Cr VI).

A summary of results of twenty pilot plant test runs is given in Table 1. The dual media filter results are also plotted in Fig. 1 and 2 for comparison with jar-test results. The majority of the tests for chromium III removal were run with Ohio River water, whereas the jar tests used only well water. All pilot plant test results for chromium III removal, alum and ferric sulfate coagulation, agreed with the jar-test results. Greater than 94 percent removals were achieved with both coagulants for all pH values (Fig. 1).

The chromium VI pilot plant studies confirmed that of the three coagulants used, only ferrous sulfate was effective for chromium VI removal. Although alum and ferric sulfate results were higher than jar-test results, chromium VI removals did not exceed 30 percent. Ferrous sulfate coagulation achieved 90 percent removal or better (Fig. 2), thereby proving to be a good coagulant for chromium VI removal.

Jar-test studies to evaluate the effect of raw water chromium III concentration showed that ferric sulfate can also achieve better removals at high concentrations than alum (Fig. 3). With 30 mg/L

*SORG, T.J. & LOGSDON, G.S. Treatment Technology to Meet the Interim Primary Water Regulations for Inorganics-Part 2. Jour. AWWA, 70:7:379 (Jul. 1979).

TABLE 2

Results of Lime Softening Pilot Plant Tests for Chromium Removal From Well Water

Test Number	Date Started	Length of Test hr	pH of Treated Water	Chromium Contaminant* Form	Chromium Contaminant* Average Raw Water Concentration mg/L	Percentage chromium Removed: Settled Water	Filtered Water: Dual Media Filter	Granular Activated Carbon Filters: Virgin GAC†	Granular Activated Carbon Filters: Exhausted GAC‡
1	11/28/77	91	9.6	Cr III	0.20	92	>98	>98	>98
2	12/12/77	87	11.3	Cr III	0.15	94	>97	>97	>97
3	12/19/77	105	9.5	Cr VI	0.13	5	5	1	5
4	3/6/78	94	9.4	Cr III	0.21	65	>98	>98	>98
5	3/13/78	96	11.0	Cr III	0.15	>97	>97	>97	>97

*Water spiked with $CrCl_3$ or $Na_2Cr_2O_7$
†Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
‡Hydrodarco 1030, ICI Americas, Inc., Wilmington, Del.

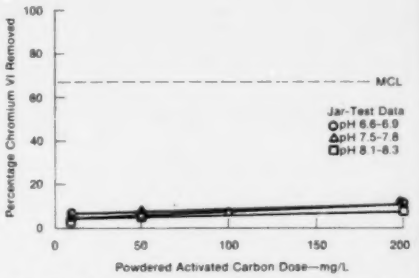

Fig. 10. Removal of Chromium VI (0.15 mg/L) From River Water by Powdered Activated Carbon

of ferric sulfate the chromium MCL (0.05 mg/L) can be attained with initial concentrations of 3.5 mg/L or less, whereas the same dose of alum is effective with concentrations of about one half this amount.

Because the literature on chromium chemistry indicates that chromium III can be oxidized to the more soluble chromium VI forms, several jar tests were conducted to determine the potential detrimental effect of prechlorination on removals. With low doses of 2 mg/L chlorine and a short contact time of 6 min, prechlorination produced no effect on chromium III removal with ferric sulfate, ferrous sulfate, and alum coagulation with turbid river water (Fig. 4).

Schroeder and Lee[14] indicate that in natural waters oxidization of chromium III is a slow process; therefore, a second alum coagulation jar test was run with higher chlorine doses and longer contact time (15 min and 24 hrs) on spiked well water having a lower chlorine demand than turbid river water. The results of this test are given in Fig. 5. Only a small decrease in removal was obtained with an increased chlorine dose and 15 min contact time. With 24 hr contact time chromium III removals decreased sharply; 10 mg/L chlorine resulted in essentially no removal.

A third jar test showed that removals are also a function of the initial chromium III concentration (Fig. 6). As expected, low doses of chlorine will react with a greater percentage of the low chromium III concentrations than of high concentrations. If ferrous sulfate is used as a coagulant instead of alum or ferric sulfate, prechlorination will have little effect because the ferrous iron–chlorine oxidization reaction probably occurs much faster than the chromium III–chlorine reaction.

Jar-test experiments were conducted for chromium VI removal with varying doses of alum and ferric sulfate (Fig. 7). Except with ferric sulfate at low pH, even very large coagulant doses of 100 mg/L did not increase removals very significantly. From a practical viewpoint, increasing the dose of alum or ferric sulfate to improve chromium VI removal provides few benefits when compared to the use of ferrous sulfate.

Ferrous sulfate is not a commonly used coagulant for drinking water treatment for two reasons: (1) alum is cheaper and readily available, and (2) the ideal pH range for ferrous sulfate is 8 to 10. Because chromium VI reduces more readily in an acid medium, increasing the pH of water immediately may be a deterrent to the ferrous iron–chromium VI reaction process. A jar test was run with pH adjustment before and after ferrous sulfate addition to evaluate the pH adjustment effect. The results are shown in Fig. 8. Below chromium VI concentrations of 1.0 mg/L, the timing of the pH adjustment showed little effect on removal. Above this level, pH adjustment prior to coagulant addition substantially lowered removal, indicating that the reduction of the chromate ion is incomplete. This phenomenon probably occurs because the ferrous iron oxidizes to ferric iron before all of the chromate is reduced. West et al[15] conducted similar jar-test experiments with wastewater and observed the same results. The addition of the coagulant before pH adjustment improved removal with high chromate concentrations.

Lime softening. Jar-test experiments showed chromium removal by lime softening is valence dependent; the results are similar to those demonstrated by conventional coagulation studies. Very high removals of 80–90 percent were achieved with chromium III, in contrast to the very low removal of less than 10 percent of chromium VI. Chromium III removal data also showed a moderate dependency on pH; removals increased from 72 percent at pH 8.5–9.5 to > 99 percent at pH 11-11.5 (Fig. 9).

Five lime softening pilot plant test runs for removing chromium from well water were conducted using the pilot plant system mentioned above. Four tests were run for chromium III removal and one for chromium VI; the test results are summarized in Table 2. The dual media filter removal results are also plotted in Fig. 9 for comparison to the jar-test results.

The chromium VI test run at pH 9.5 verified the inability of lime softening to remove chromium VI; only 5 percent removal was achieved. Two test runs at pH 11.0 and 11.3 for chromium III removal confirmed the good removal results obtained by jar testing of 97 percent or more. The removal results for two lower pH test runs, pH 9.4 and 9.6, were significantly higher than the laboratory test results. Pilot plant removals were 97 percent or better, in contrast to the 70 percent removal achieved by jar testing. The pilot plant testing did not verify the pH effect observed during the laboratory tests.

The literature on the treatment of municipal and industrial wastewaters indicates that very high removals comparable to the pilot plant results should occur with chromium III by lime softening. The reason for lower removals at pH 8.5 to 10.5 achieved in the jar-test experiments is not known.

Jar-test experiments at optimum pH for removal of high chromium III concentrations indicated that lime softening is more effective than either alum or ferric sulfate coagulation (Fig. 3). For example, lime softening was shown to achieve the chromium MCL when the initial concentration was as high as 10 mg/L. Ferric sulfate and alum were as effective with concentrations about 3.5 mg/L and 1.5 mg/L, respectively.

Ion exchange. Because chromium is not a problem in drinking water, no real need has existed for studying its removal from drinking water by ion exchange. Wastewater technology, principally industrial waste treatment, indicates that ion

exchange could be applied successfully for chromium removal from drinking water, if required. Cation resins can be utilized for chromium III removal, and anion exchange resins will remove chromium VI. From an economical and operational viewpoint, ion exchange may not be a very useful method for removing low chromium concentrations from drinking water, because pH is a critical factor in removal capacity.

Miller and Mindler[19] report that chromium III and VI contamination of rinse waters of the metal plating industry can be removed by a standard two-step ion exchange process: a strong acid cation resin removing chromium III followed by a strong base anion resin removing chromium VI. These resins are regenerated with sulfuric or hydrochloric acid (cation resin) and sodium hydroxide (anion resin), chemicals that are expensive and hazardous to handle. Strong base resins in the chloride form are also used to remove chromium from cooling tower blowdown water. Best removals are achieved at pH 4.5 to 5 where the dichromate ion is prevalent. Two ion exchange sites are required for the removal of either chromate (CrO_4^{-2}) or dichromate ($Cr_2O_7^{-2}$). Operating in an acid environment takes advantage of the capacity increase by loading with dichromate rather than chromate; two rather than one chromium ions are removed at each double site. Several methods of operation are available to make use of this capacity factor: (1) the water can be adjusted to the proper pH before treatment, and (2) the chromate ion can be removed at a higher pH and the bed can be acidified later to convert the chromate to the dichromate form, thereby providing additional sites for loading. Because some chromate leakage occurs above pH 4.5–5, the first method is preferred for treating industrial wastewaters.

Unless the water source is very high in chromium, pH adjustment would be impractical for treating drinking water. Chromium VI can be removed at a higher pH, but high efficiency could not be achieved. Linstedt et al[20] showed that trace amounts of 0.05 mg/L chromium VI could be removed (96 percent) from secondary effluent with cation and anion exchangers in series. As expected, 91 percent of the chromium was removed by the anion resin.

Activated carbon. The literature on the removal of chromium from water by activated carbon has been recently summarized by Huang.[21] Laboratory studies for chromium VI removal with powdered activated carbon (PAC) and granular activated carbon (GAC) constitute much of the present research effort.

Huang and Wu[22] conducted batch tests to evaluate the effect of pH and initial chromium concentration on the removal of chromium VI with GAC.* With a GAC dose of 10 000 mg/L, removals increased with increasing pH from pH 2 to pH 5–6, at which point removals declined rapidly with increasing pH. Chromium VI adsorption also increased with the initial chromium concentration. Huang and Wu reported that some chromium VI is reduced to chromium III in the presence of GAC, but the reduction reaction only occurred below pH 6.

Huang and Wu showed that chromium III is also adsorbed by GAC, but to a lesser extent than chromium VI. The highest removal occurs at pH 5. No appreciable adsorption occurred below pH 2.8 or above pH 6.0.

Netzer and Norman[23] conducted laboratory studies over a pH range of 3 to 11 with high doses of 10 000 mg/L PAC† for the removal of chromium III from wastewater. Test results were somewhat similar to those of Huang and Wu. Best removals were achieved at pH 3 to 5. At a higher pH some chromium is also adsorbed, but most of the chromium is removed by pH adjustment forming insoluble chromium III compounds.

A third study reported by Yoshida et al[24] concerns the adsorption of 10 mg/L chromium III and VI onto PAC and GAC as a function of pH. Chromium VI was readily adsorbed by both types of activated carbon in the 4–6.5 pH range as the $HCrO_4^-$ and CrO_4^{-2}. Chromium III was not adsorbed at any pH by GAC, and in acid solution chromium VI was easily reduced to chromium III in the presence of activated carbon.

The DWRD conducted several jar-test studies using lower doses of 10–200 mg/L PAC† for removal of chromium VI (0.15 mg/L) from Ohio River water. Test results showed very low removals from pH 6.8 to pH 8.3 (Fig. 10). Although some improvement was achieved with increasing doses of PAC, total removal with a 200 mg/L dose was less than 13 percent. These data indicate that PAC treatment of drinking water for taste and odor control would not be useful for chromium VI removal.

The effectiveness of GAC for the removal of low concentrations of chromium VI from wastewater has been studied in pilot plant systems by Linstedt et al[20] and Maruyama et al.[25] Test results from both studies that consisted of GAC treatment following sand filtration showed removals achieved by sand filtration of 2.5 percent (Linstedt et al) and about 50 percent (Maruyama et al). Cumulative removals of chromium following GAC treatment were significantly higher at 96.6 percent and 98 percent, respectively. Linstedt et al speculated that the high removals achieved by GAC might result from a direct chemical interaction between organic substances in wastewater and chromium VI, subsequent removal of the organics on the carbon.

The DWRD pilot plant data of Tables 1 and 2 support the suggestion of Linstedt et al; the vast majority of chromium VI removal results by GAC were essentially the same as those achieved by sand filtration. The DWRD tests were conducted with a drinking water source that has significantly lower levels of organic material than wastewater. These data suggest that GAC treatment probably is not a very effective method for chromium VI removal from drinking water with low organic concentrations. Furthermore, the laboratory studies also indicated that GAC is effective for chromium VI removal only in the pH range of 5–6 and not at pH 7–8, the range in which these tests were conducted.

Reverse osmosis and electrodialysis. Mixon[26] conducted laboratory reverse osmosis (RO) studies for the removal of chromium VI from a variety of potable waters, wastewaters, and brackish waters using several RO membranes. Long- and short-term studies were run, and chromium concentrations varied from 0.94 to as high as 10.0 mg/L. When the chromium concentrations were less than 5 mg/L, chromium rejections ranged from about 93 to 99 percent regardless of the type of water or membrane. Slightly lower removals of 83 to 85 percent were achieved only when chromium concentrations increased to nearly 10 mg/L.

Hindin et al[27] also ran laboratory tests using a small cellulose acetate (CA) RO membrane cell on aqueous solutions spiked with chromium VI. Rejection results were equal to or better than those achieved by Mixon. Removals of 96.7, 95.0, and 93.5 percent were achieved with initial raw water concentrations of 0.47, 5.0, and 49.6 mg/L, respectively.

Chromium III removal from distilled water and secondary wastewater effluent by RO was studied by Johnston and Lim[28] using a small laboratory unit and a 4.54 m^3/day pilot plant system. The laboratory RO static test cell containing a CA membrane achieved greater than 99 percent rejection of 10 mg/L of chromium III. When the system was stressed with 100 and 1000 mg/L of chromium, the unit continued to produce very good results at 97.3 and 94.8 percent, respectively. The pilot plant system studies also showed excellent results. Greater than 99 percent rejection was obtained with concentrations from 0.15 to 7.3 mg/L.

A general literature review did not reveal any specific data on the removal of chromium from drinking water by electrodialysis. Because of the similarities in treatment capabilities, this technique should be as effective as RO.

Chromium treatment summary. Chromium III is very insoluble in alkaline

*Filtrasorb 400, Calgon Corp., Pittsburgh, Pa.
†Nuchar Aqua A, Westvaco Corp., Covington, Va.

solutions, and therefore conventional coagulation and lime softening are effective removal techniques. At pH 7 and above, alum and iron coagulants can achieve better than 90 percent removal. Lime softening can obtain even higher reductions of 95 percent or greater at pH 10.7 and above.

When coagulant doses of 30 mg/L are used in conventional treatment, the chromium MCL of 0.05 mg/L is attainable with raw water chromium III concentrations up to about 1.5 mg/L for alum coagulation and up to 3.5 mg/L for iron coagulation. Lime softening at pH 10.7 or higher is capable of achieveing the MCL with drinking waters containing 10 mg/L of chromium III.

Chromium VI is very soluble in aqueous solutions, and therefore neither alum or ferric sulfate coagulation nor lime softening are good treatment methods for its removal. Chromium VI can be removed from water by converting it to the trivalent form using ferrous sulfate as a coagulant. As the ferrous ion oxidizes to the ferric ion, chromium VI is reduced to the insoluble chromium III form. Thus, ferrous sulfate coagulation is a good technique for chromium VI removal from drinking water.

Ion exchange treatment using a cation resin for chromium III and an anion resin for chromium VI is effective for removing chromium from drinking water. Although this technique has been used in treating industrial wastewaters, the method is not very practical for drinking water because two types of resins are required. Moreover, pH is critical for chromium VI removal. The best results are achieved at pH 4.5 to 5 where the dichromate ion is prevalent.

Laboratory and pilot plant studies show that neither PAC nor GAC is very practical for chromium VI removal. PAC doses commonly used for taste and odor control will remove only very small quantities of chromium VI and only at low pH. GAC treatment has been demonstrated to achieve high chromium VI removal of 90–100 percent from wastewaters that contain high amounts of organic material, but little or no removal from water with low organic content.

Laboratory data indicate that excellent removal of chromium III and VI can be achieved by reverse osmosis. Electrodialysis is comparable to RO and therefore should also be a good technique for the reduction of both forms of chromium from drinking water.

Because chromium is not a common problem in drinking water and can be easily removed from water by conventional treatment, DWRD plans little further research on its removal.

Mercury Removal From Water

Health effects. Mercury was introduced in the federal drinking water standards in the 1975 NIPDWR. The decision to place mercury (with an MCL of 0.002 mg/L) into the drinking water regulations was made because mercury is a very toxic chemical, and the chances of mercury occurring in drinking water have greatly increased over the last decade.

Mercury occurs in inorganic and organic forms, both of which are toxic to humans. In the inorganic form the mercurous salts (monovalent) are less soluble than mercuric salts (divalent) and are consequently less acutely toxic. The fatal dose of mercuric salts ranges from 20 mg to 3 g.[29] Chronic inorganic mercury poisoning is often associated with industrial exposure, whereas organic mercury poisoning results more from accidents or environmental contamination. The symptoms of chronic inorganic mercury poisoning consist first of headaches, giddiness, and reduction in perception. Fine tremors gradually develop in the hands and are intensifed when movement is begun. Prolonged and severe intoxication results in a mixture of fine and coarse tremors; as the illness progresses, nervous restlessness appears that is characterized by psychic and emotional distress and even hysteria.

Organic mercury, particularly the alkyl compounds, is more toxic to man than the inorganic forms, and ingesting only a few milligrams will produce illness. Chronic alkyl mercury poisoning, known as Minamata disease, may appear after a few days or a few years of exposure. Poisoning is characterized mainly by neurological symptoms and leads to permanent damage or death. The largest outbreak of Minamata disease occurred from 1953 to 1960 in a village near Minamata Bay, Japan, where 121 people were affected (46 died) by ingestion of fish containing high concentrations of methyl mercury.[31]

A very significant factor in mercury poisoning is the absorption factor. Methyl mercury has been estimated to be absorbed at more than a 90 percent rate in the gastrointestinal tract as compared with 2 percent for mercuric ion.[32] Methyl mercury also crosses the placenta into the fetus and achieves a 30 percent higher concentration in fetal erythrocytis than in maternal red blood cells.[33]

Epidemiologic evidence shows that the lowest whole-blood concentration of methyl mercury associated with toxic symptoms is 0.2 μg/L.[34] This value corresponds to prolonged, continuous exposure at approximately 0.3 mg Hg/70 kg body weight/day. To provide a safety factor of ten, the maximum intake should be no more than 0.03 mg Hg/person/day. Estimating the dietary intake of mercury at 0.01 mg/L[7] and 0.004 mg/L from two litres of drinking water, the MCL presently provides a considerable factor of safety. Persons regularly consuming contaminated fish may exceed the estimated food intake limit by three or four times, but even under these conditions a reasonable safety factor exists with the MCL at 0.002 mg/L.

The NAS[7] reviewed the background information for the MCL regulation and questioned the need and usefulness of a mercury standard in drinking water because the potential hazard of very low levels of methyl mercury in US drinking water is inconsequential when compared to the contribution from food. The academy agreed, however, that the lack of firm data on the ratio of organic mercury to total mercury in drinking water supports the need to limit mercury in drinking water on the basis that all of it is methyl mercury. Currently, the general opinion is that mercury exists principally in the inorganic form in drinking water. Because this opinion has not been firmly substantiated, the NAS recommended that specific investigations be conducted to validate or modify it.

Very little historical data have been developed on the occurrence of mercury in ground, surface, or finished waters. Essentially no information was developed before 1970. For example, neither the five-year summary (1962–1967) of Trace Metals in Rivers and Lakes of the US[10] nor the 1969 Survey of Community Water Supply[12] included any information on mercury.

In 1970 the USGS conducted a nationwide survey of minor elements including mercury in US surface waters of the 50 states.[11] These data show only 7 percent of 720 water samples contained mercury above the detection limit of 0.0001 mg/L. The maximum concentration was only 0.0043 mg/L. Because mercury is one of the least abundant elements in the earth's crust, it should not be frequently found in natural groundwaters. Consequently, potential problems lie mainly with surface waters receiving wastewater from industrial or manufacturing processes using mercury. The major use of mercury in the US is as a cathode in the electrolytic preparation of chlorine and caustic soda (33 percent). Other major groups of industries using mercury are those producing electrical apparatus and control instruments.

The PHS–EPA interstate carrier water supply certification program inserted the mercury analysis in the routine sampling schedule in 1970. The 1973 summary report[35] on the chemical analysis of interstate carrier water supply systems showed only six of 389 finished water samples (1.5 percent) exceeding the MCL of 0.002 mg/L; the maximum concentration found was 0.005 mg/L. The last report in April 1975[36] showed a slight increase in occurrence. Thirteen water samples in a total 512 samples (2.5 percent) exceeded the MCL, and the maximum level was 0.5 mg/L. Thirty-

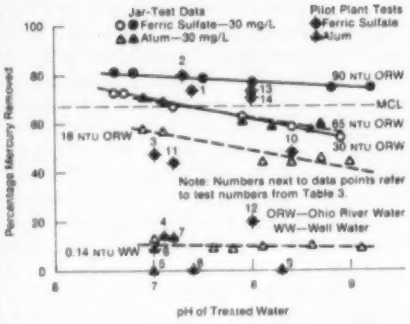

Fig. 11. Effect of pH and Turbidity on Inorganic Mercury (0.006 mg/L) Removal by Coagulation Treatment

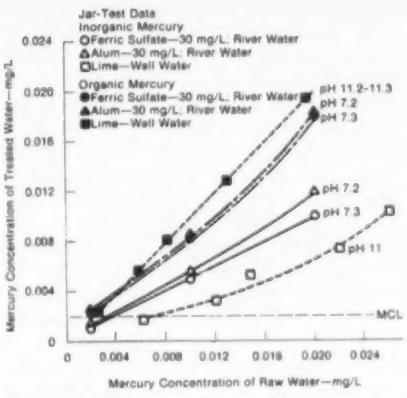

Fig. 12. Effect of Initial Concentration on Mercury Removal by Coagulation and Lime Softening Treatment

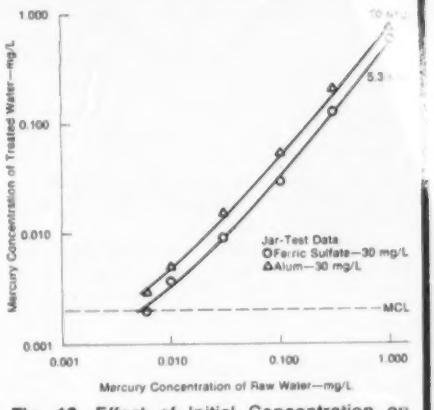

Fig. 13. Effect of Initial Concentration on Inorganic Mercury Removal From River Water by Conventional Coagulation

TABLE 3

Results of Conventional Coagulation Pilot Plant Tests for Inorganic Mercury Removal

Test Number	Date Started	Length of Test hr	Test Water	Coagulant Type	Coagulant Dose mg/L	pH of Treated Water	Turbidity of Raw Water* NTU	Average Raw† Water Mercury Concentration mg/L	Percentage Mercury Removed: Settled Water	Filtered Water: Dual Media Filter	Granular Activated Carbon Filters: Virgin GAC‡	Exhausted GAC‡	Virgin GAC§
1	12/12/73	35	Cincinnati tap	ferric sulfate	45	7.4	11	0.005	64	74	–	–	–
2	12/19/73	41	Cincinnati tap	ferric sulfate	72	7.3	11	0.006	70	80	–	–	–
3	1/8/74	40	Cincinnati tap	ferric sulfate	34	7.0	7	0.0045	38	48	–	–	–
4	1/21/74	100	Cincinnati tap	alum	22	7.1	13	0.006	5	15	–	–	–
5	1/28/74	102	Cincinnati tap	alum	21	7.0	13	0.006	2	0	–	–	–
6	2/4/74	103	Cincinnati tap	alum	41	7.0	13	0.0075	3	9	–	–	–
7	3/4/74	100	Cincinnati tap	alum	62	7.2	13	0.0055	0	14	–	–	–
8	11/11/74	101	Cincinnati tap	alum	26	7.4	<1	0.0048	0	0	–	–	–
9	11/18/74	102	Cincinnati tap	alum	26	8.3	<1	0.005	0	0	–	–	–
10	12/16/74	101	Cincinnati tap	ferric sulfate	15	7.2	<1	0.006	24	44	–	–	–
11	12/18/74	102	Cincinnati tap	ferric sulfate	19	8.4	<1	0.006	36	47	–	–	–
12	2/7/77	93	Ohio River	ferric sulfate	28	8.0	5	0.0055	13	20	55	49	–
13	5/9/77	99	Ohio River	alum	30	8.0	31-76	0.007	63	74	–	87	>93
14	9/12/77	91	Ohio River	ferric sulfate	29	8.1	10-20	0.008	73	73	–	80	88

*Turbidity of tap water adjusted with bentonite clay
†Raw water spiked with HgCl,
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
§Hydrodarco 1030, ICI Americas, Inc., Wilmington, Del.

TABLE 4

Results of Conventional Coagulation and PAC Pilot Plant Tests for Organic Mercury Removal

Test Number	Date Started	Length of Test hr	Test Water	Coagulant Type	Coagulant Dose mg/L	PAC Dose mg/L	pH of Treated Water	Turbidity of Raw Water NTU	Average Raw* Water Mercury Concentration mg/L	Percentage Mercury Removed†: Settled Water	Filtered Water: Dual Media Filter	Granular Activated Carbon Filter: Virgin‡ GAC	Virgin§ GAC	Exhausted** GAC
1	5/13/74	54	Cincinnati tap	ferric sulfate	31	9††	7.0	<1.0	0.0054	24	31	100	100	86
2	5/15/74	54	Cincinnati tap	ferric sulfate	31	17††	7.0	<1.0	0.0045	32	38	99	100	98
3	5/20/74	57	Cincinnati tap	ferric sulfate	35	7‡‡	7.0	<1.0	0.0056	27	40	100	100	98
4	5/23/74	40	Cincinnati tap	ferric sulfate	28	7‡‡	7.0	<1.0	0.0055	5	8	100	100	99
5	6/3/74	61	Cincinnati tap	ferric sulfate	28	0	6.8	<1.0	0.0037	0	19	100	97	84

*Water spiked with CH HgCl
†Detectable limit of 0.0005 mg/L was used to compute percentage where effluent was at or below detectable limit; value reported with > symbol.
‡Hydrodarco 1030, ICI Americas, Inc., Wilmington, Del.
§Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.
**Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.
††Darco-B, ICI Americas, Inc., Wilmington, Del.
‡‡Darco-M, ICI Americas, Inc., Wilmington, Del.

two and 39 other samples in 1973 and 1975, respectively, were possible failures because the minimum detectable limit was higher than the MCL. Although the mercury data base is small and an increase in occurrence took place between 1973 and 1975, these data and the mercury data on lakes and rivers indicate that mercury in water is not now a serious problem and probably will not be in the near future.

Mercury chemistry overview. Mercury has three basic oxidation states in aqueous solutions: (1) the pure metal, Hg^0; (2) the monovalent (mercurous), H^+; and (3) the divalent (mercuric), Hg^{+2}. Besides forming the common inorganic salts, mercury has the unique capacity among metals of forming organic complexes, the most significant being the very toxic methyl mercury ion, CH_3Hg^+.

Gavis and Ferguson[37] and Hem[38] have reported on the existence of inorganic mercury species in natural waters. As expected, the nature and concentration of the mercury species depends upon the oxidation-reduction characteristics and the pH of the water and upon the nature of the anions and other groups present. These authors show, in Eh-pH diagrams for mercury in equilibrium water containing chloride and sulfur anions, that the most significant species are Hg^0 (metallic mercury) and the divalent complexes $HgCl_2$ and $Hg(OH)_2$.

The most predominant mercury species in water having a pH above five and moderate oxidizing conditions is metallic mercury. The solubility of the pure metal is relatively low, about 0.025 mg/L, which is the concentration considered the probable upper limit of mercury in surface waters low in chloride.[38] In oxygenated waters with high chloride concentrations, the solubility of mercury increases with the formation of the uncharged $HgCl_2$ and $Hg(OH)_2$ species. In mildly reducing conditions mercury can be precipitated as the sulfide and thereby immobilized, but in a very strong reducing environment the solubility increases because the divalent ion can convert to the very soluble free metal.

Metallic mercury is more soluble in organic solvents than in water. Mercury forms organic complexes, and some of these species are also relatively soluble in water. The most significant organic mercury complex is methyl mercury, CH_3Hg^+, which has been found in fish and other food products of animal origin. Methylation of inorganic mercury (metallic and divalent forms) in solution by bacteria living in the sediment of lakes and streams has been documented.[39,40] Methyl mercury is soluble in low concentrations and therefore can escape into the water above the bottom sediment layers by turbulent and convective motions of the water. Apparently, aquatic organisms can extract methyl mercury compounds from water, and the higher the organism in the food chain, such as fish, the greater the concentration of methyl mercury in its tissues. Gravis and Ferguson[37] and Hem[38] agree that there are many gaps and unanswered questions in the knowledge of methylation and aquatic organisms' uptake of mercury compounds in natural waters. The process may be very slow. Consequently, a mercury problem may not occur in a water supply until many years after the introduction of mercury into its source.

Another important characteristic of mercury which has application to water treatment is the tendency for mercury to adsorb and adhere to various types of materials. As most laboratory workers know, mercury and its compounds will adhere to glassware. Krauskopf[41] has also shown that divalent mercury can be adsorbed from seawater with iron oxides and clay. The concentration of mercury in sediment material in the bottom of lakes and streams further indicates the adsorption capability of mercury onto natural organic materials. This information suggests that both inorganic and organic mercury should adsorb onto natural turbidity and be removed to some degree by conventional coagulation treatment.

Treatment methods. Shortly after the Minamata Bay[42] incident that triggered a worldwide concern for mercury contamination, research was begun on methods for removing mercury from drinking water. The treatment techniques studied most extensively have been conventional coagulation, lime softening, and activated carbon. Ion exchange and reverse osmosis have also been investigated to a lesser degree.

Conventional coagulation. Two of the earliest reported studies on mercury removal from drinking water were by Ebersole and O'Connor[43] and Logsdon and Symons.[44] Ebersole and O'Connor investigated the effect of pH, coagulants, polyelectrolytes, and adsorbents on inorganic mercury removal from spiked tap water; Logsdon and Symons studied the influence of turbidity, coagulant, coagulant dose, and contaminant concentration on both inorganic and organic mercury. Their data, developed from jar tests, indicate that mercury removal is dependent to some degree on all of the factors studied (except for initial concentration) in the 0.003-0.016 mg/L range.

Ebersole and O'Connor[43] found pH to be very significant for iron coagulation, and to a lesser extent for alum coagulation. For example, iron removals increased from 30 percent at pH 6 to near 100 percent at pH 8, and then decreased to about 60 percent at pH 10. Alum coagulation was much less effective; at pH 6 and 10 removal was 25 percent, and the maximum removal was slightly less than 50 percent at pH 7. The initial mercury concentration used was 0.050 mg/L. Thus, 96 percent removal was necessary to meet the 0.002 mg/L MCL.

The DWRD recently conducted jar tests to study the effect of pH on river water and groundwater spiked with inorganic mercury three times the MCL (0.006 mg/L). These test data are plotted in Fig. 11 and show a very small pH trend; removals by alum and iron coagulation decreased very slightly as pH increased from 6.5 to 9. Furthermore, in no test did removals approach the 100 percent achieved by Ebersole and O'Connor. The highest removals obtained were about 80 percent. The mercury solubility curve (Hg^{+}-$HgOH^{+}$) by Singer[45] shows a trend similar to Fig. 11 where mercury solubility decreases with increasing pH.

Although pH appeared not to be significant for inorganic removal, the data of Fig. 11 indicate that the type of coagulant and the turbidity of the raw water are important. These results are consistent with those reported in the two studies mentioned above. At approximately the same level of turbidity, iron is more effective than alum. As the turbidity increases, mercury removal increases irrespective of the coagulant employed. These data, therefore, suggest that inorganic mercury should be easier to remove from turbid surface waters than from low turbidity groundwaters by conventional treatment.

Logsdon and Symons[44] reported that turbidity had a much more pronounced effect with alum coagulation than with iron coagulation. For example, when the turbidity was 3 NTU only 10 percent was removed, but with 100 NTU mercury reduction was about 60 percent. By contrast, iron removal increased from about 50 to only 55 percent as the turbidity increased from about 2 to 100 NTU. These authors also showed that methyl mercury removals increased with increasing turbidity from 2-100 NTU, but total removals were always less than inorganic removal.

Some removal of inorganic and methyl mercury can be achieved by removal of natural turbidity by clarification without using a coagulant.[44] As expected, the amount of removal is dependent on turbidity; the higher the turbidity, the greater the percent removal.

The DWRD conducted several pilot plant studies to compare mercury removals to the jar-test results. The summary results of fourteen inorganic mercury tests are given in Table 3 and of five methyl mercury tests in Table 4. The majority of the tests were conducted with Cincinnati tap water, because the tests were conducted with the DWRD pilot plant before the water tank trailer was available for hauling water. In order to evaluate the turbidity effect, bentonite clay was added to the tap water to increase the turbidity. The coagulant

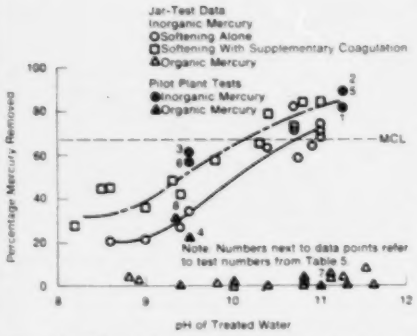

Fig. 14. Effect of pH on Mercury (0.003–0.19 mg/L) Removal by Lime Softening

TABLE 5

Results of Lime Softening Pilot Plant Tests for Mercury Removal From Well Water

Test No.	Date Started	Length of Test hr	pH of Treated Water	Mercury Contaminant* Form	Mercury Contaminant* Average Raw Water Concentration mg/L	Percentage Mercury Removed: Settled Water 1st Stage	Settled Water 2nd Stage	Filtered Water: Dual Media Filter	Filtered Water: Granular Activated Carbon Filters: Virgin GAC†	Virgin GAC‡	Exhausted GAC‡
1	1/20/75	97	11.3	inorganic	0.004	63	80	81	92	–	–
2	2/3/75	100	11.3	inorganic	0.003	88	–	89	>95	–	–
3	2/10/75	10[illegible]	9.5	inorganic	0.0027	46	–	61	>95	–	–
4	3/3/75	59	9.5	organic	0.0026	30	–	22	>98	–	–
5	3/31/75	95	11.3	inorganic	0.0057	77	–	89	>97	–	–
6	4/7/75	101	9.5	inorganic	0.0044	39	–	57	>97	–	–
7	3/13/78	93	11.0	organic	0.0039	0	–	0	–	>86	80
8	3/20/78	90	9.4	organic	0.0054	30	–	31	–	88	80

*Raw water spiked with either $HgCl_2$ or CH_3HgCl
†Filtrasorb 100, Calgon Corp., Pittsburgh, Pa.
‡Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.

dose and pH were also varied; an iron dose as high as 72 mg/L was used in one test run. The test results show that mercury removals were similar to those achieved by jar testing: (1) iron was more effective than alum, and (2) the higher the turbidity, the greater the removal. The dual media filter results of Table 3 are plotted on Fig. 11 to compare pilot plant and jar-test results.

Because of the very low limit of mercury in drinking water, the effect of initial concentration is significant. Logsdon and Symons[44] report that the percentage of removal is not affected by the initial concentration in the 0.003 to 0.016 mg/L range when coagulant doses of 20 to 30 mg/L are used. When their test data are plotted to show the mercury residual concentration in the treated water (Fig. 12), the initial concentration is significant. The data very clearly demonstrate that conventional coagulation, using 30 mg/L of a coagulant, is an effective method of achieving the MCL only for very low levels (0.003–0.004 mg/L) of inorganic mercury and is ineffective for organic mercury.

DWRD conducted additional tests for inorganic mercury removal with spiked concentrations up to 10 mg/L. The test data, plotted in Fig. 13, confirm the results of the earlier experiments (Fig. 12). Under the test conditions imposed, the MCL is achieved only if the initial concentration does not exceed about 0.003 mg/L for alum coagulation and about 0.006 mg/L for iron coagulation. For higher mercury concentrations, either the treatment conditions must be altered or another method employed.

Lime softening. Logsdon and Symons[44] evaluated the pH effect for removal of mercury (0.002–0.019 mg/L) by lime softening from pH 9.4 to 11.5 using jar-test procedures. The results are plotted in Fig. 14 and show that pH had no effect on methyl mercury; essentially no removal was achieved by the process throughout the entire pH range. Inorganic mercury removal ranged from 60 to 70 percent at pH 10.7–11.1 and then decreased with decreasing pH to near 30 percent removal at pH 9.4. Supplementary iron coagulation was attempted with lime softening to improve removal. The combination of lime and iron increased inorganic mercury removal in the lower end of the pH range (pH 9.5–10.5) by 10–15 percent and about 5–10 percent above this range. Again, no methyl mercury was removed by this process.

The jar-test data were also plotted on the basis of residual mercury concentration vs raw water concentration (Fig. 12). Because organic mercury is not removed, the curve has a slope of 45 degrees. The inorganic mercury plot clearly shows that lime softening is a better method than either alum or ferris sulfate coagulation, but it is only capable of achieving MCL levels when the raw water concentration is 0.006–0.007 mg/L or less.

Several pilot plant tests were conducted for comparison to the jar-test results. The results of five test runs for inorganic mercury removal and three tests for methyl mercury removal are given in Table 5 and the dual media filter results plotted in Fig. 14 for comparison to jar-test results. Except for test 7 when methyl mercury removal was zero, dual media filter removals were higher than jar-test removals. The largest difference occurred with inorganic mercury at low pH (tests 3 and 6). Pilot plant removals were 61 and 57 percent as compared to jar-test removals of 30 to 40 percent. One possible reason for the difference is that the measured raw water mercury concentrations were approximately one half the theoretical feed concentration. If the theoretical spiked concentration of 0.006–0.007 mg/L is used to calculate percentage removal, the pilot plant results are similar to jar-test results. No explanation is known for the differences between results obtained with spiked and measured concentrations of the pilot plant raw water.

Ion exchange. Ion exchange technology for mercury removal has been limited to treating industrial wastewater. The application in this field has been confined primarily to the removal of inorganic mercury in the mercury chloride form by anion resins. For the process to be effective, the chloride content of the wastewater must be high; if it is low, either chlorine or a chloride salt is added to improve the removal process. Patterson's[45] review of ion exchange treatment of industrial wastewaters indicates the best results are achieved from a two-stage process: a roughing stage followed by a second, polishing ion exchange unit to bring the mercury level down to 0.001 to 0.005 mg/L. The pH of the process is also important, with the preferred pH being neutral to slightly acidic.

Cation exchange of mercury may be effective when the chloride content is low and mercury is in the metallic form. Patterson states that cation exchange behavior of mercury is rare, but several resins* are reported to be effective. One manufacturer[47] also indicates that the relative affinity of mercury (Hg^{+2}) for a strong acid cation exchanger is higher than that of calcium but slightly less than those of barium and lead. Patterson[45] and Calmon[48] indicate that methyl mercury

*Amberlite IR-120, Rohm & Haas Co., Philadelphia, Pa., and Dowey-50W-X8, Dow Chemical Co., Midland, Mich.

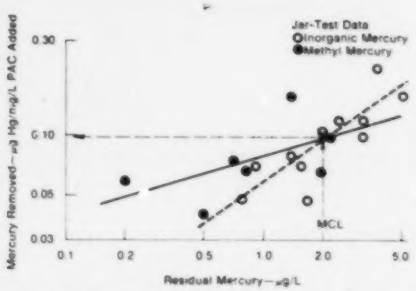

Fig. 15. Freundlich Isotherms for Mercury Adsorption With PAC[44]

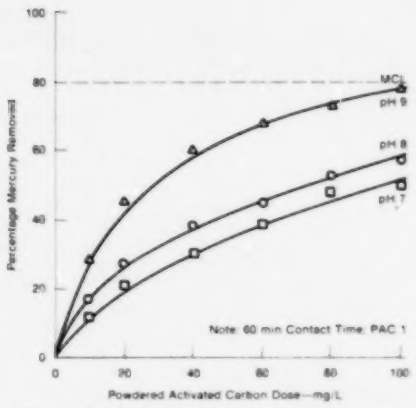

Fig. 16. Effect of pH on Removal of Inorganic Mercury (0.010 mg/L) With PAC Treatment[44]

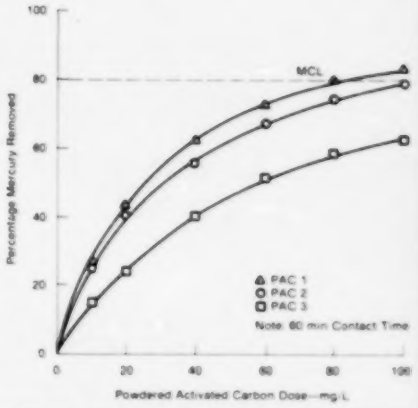

Fig. 17. Removal of Methyl Mercury (0.010 mg/L as Hg) by PAC at pH 7[44]

may be removed with anion exchange technology, but information is lacking on the removal of most organic mercury complexes.

Applying ion exchange technology for mercury removal from drinking water is probably not practical. The limited data on industrial use indicate that the selection of the ion exchange resin is dependent on the mercury form. Because of the potential for mixed or changing forms of mercury in drinking water sources, design of an efficient ion exchange system would be extremely difficult.

Activated carbon. Several investigations have been conducted on the use of powdered and granular activated carbon for the removal of both inorganic and organic mercury from water. Logsdon and Symons[44] conducted jar tests on the removal of low concentrations (~0.009 mg/L) of both mercury forms from spiked, low turbidity tap water with PAC.* The results of the inorganic tests showed that increasing doses of PAC decreased the residual mercury concentration after treatment. When plotted as a Freundlich isotherm (Fig. 15), the data show that in achieving the MCL of 0.002 mg/L, each mg/L of PAC removes 0.0001 mg of inorganic mercury.

The organic mercury results were similar. The activated carbon efficiency at the MCL was identical to the inorganic mercury result of 0.0001 mg of mercury removed for each mg/L of PAC added. Although the activated carbon efficiency for the removal of both mercury forms was identical for achieving the MCL, a comparison of the slopes of the two isotherm curves indicated that PAC was slightly more efficient for inorganic mercury above the MCL residual value; for organic mercury, below the MCL.

Activated carbon adsorption is generally pH dependent for metal removal; adsorption increases with decreasing pH. Thiem and O'Connor[45] and Humenick and Schnoor[36] studied the pH effect and found this characteristic to apply to mercury. Thiem and O'Connor evaluated several different types of active carbon for the removal of inorganic and organic mercury at 0.010 mg/L from a simulated drinking water at pH 7, 8, and 9. The inorganic tests were performed with a lignite-based PAC,* and the results exhibit a dramatic pH effect on removal (Fig. 16). At the lower range of PAC dosages, mercury removal was reduced by nearly one half as the pH was raised from 7 to 9.

Humenick and Schnoor[36] conducted batch tests for adsorption isotherms at pH 4 and 10 using much higher inorganic mercury concentrations of 10 mg/L. A comparison of the isotherm data for 1 mg/L residual mercury shows the PAC† capacity was 0.14 mg Hg/g activated carbon at pH 10, whereas at pH 4 the capacity was almost 10 times higher at 1.0 mg Hg/g activated carbon.

The methyl mercury (0.010 mg/L) removal at pH 7, 8, and 9 was carried out with three different activated carbon base materials: (1) PAC 1,* a lignite base; (2) PAC 2,‡ a petroleum base; and (3) PAC 3,§ a bituminous base.[45] With the exception of PAC 3, methyl mercury removals decreased as the pH was increased from 7 to 9. Mercury reduction with PAC 3 was identical at pH 7 and 8 and decreased at pH 9. The effectiveness of the three materials within the pH range of 7 to 9 were in the order of PAC 1 > PAC 2 > PAC 3. At pH 7 and a PAC dose of 100 mg/L, PAC 1 removed 82 percent, PAC 2 removed 78 percent, and PAC 3 removed 62 percent (Fig. 17).

PAC can be used with conventional coagulation treatment to enhance mercury removals. Logsdon and Symons[44] showed that 65 mg/L of PAC* plus 30 mg/L of alum achieved an inorganic mercury reduction in excess of 70 percent, as compared to about 40 percent removal obtained with alum alone with Ohio River water. Ebersole and O'Connor[45] also reported that PAC† in conjunction with either alum or iron coagulants improved inorganic mercury removal. For example, their studies with tap water containing 0.50 mg/L of inorganic mercury showed 30 mg/L of PAC increased alum removals from 35 to 73 percent, and a 20 mg/L dose raised iron removals from 67 to 85 percent.

DWRD conducted several pilot plant tests to evaluate the additional benefits of PAC with conventional treatment for methyl mercury removal. Five experiments were conducted using Cincinnati tap water spiked with 0.0037 to 0.0056 mg/L of mercury. During the first four test runs PAC was added with ferric sulfate in the rapid mix tanks of the pilot plant system. Two types of PAC were used and the doses ranged from 7 to 17 mg/L. For comparison, no PAC was added during the last test run. The test data show that even low doses of PAC may improve organic mercury removal when used in combination with an iron coagulant (Table 4). When PAC was

*Nuchar Aqua A, Westvaco Corp., Covington, Va.

*Darco HDB, ICI Americas, Inc., Wilmington, Del.
†Filtrasorb 300, Calgon Corp., Pittsburgh, Pa.
‡Amoco PX-21, Amoco Research Corp., Chicago, Ill.
§Nuchar Aqua, Westvaco Corp. Covington, Va.

*Nuchar Aqua A, Westvaco Corp., Covington, Va.
†Nuchar W-C1000-N, Westvaco Corp., Covington, Va.

added, settled water removals ranged from 5 to 32 percent and dual media removals from 8 to 40 percent. With no PAC, mercury removal was zero percent for settled water and 19 percent for the filtered water.

The capacity of GAC* for mercury removal was evaluated by Logsdon and Symons[31] by pumping 0.020–0.029 mg/L mercury solutions through GAC filter columns for various periods ranging from days to weeks with empty contact times of 0.4 to 3.5 min. The results of the column tests showed that removals decreased with the amount of water treated and that contact time was significant; the longer the contact time, the greater the capacity and percentage removal. As expected, the GAC showed a greater capacity for organic mercury than for inorganic mercury; the longer the contact time, the greater the difference in capacity between the two forms. Columns with empty bed contact times of approximately 3.5 min removed 80 percent of inorganic mercury for 15 000 bed volumes and 80 percent of organic mercury for 25 000 bed volumes treated.

Sigworth and Smith[11] also reported on a GAC column test (2.5 cm ID by 30 cm) for removal of methyl mercury [0.025–0.050 mg/L (as Hg)] from tap water containing mercury. Over a three-month period, removals were between 90 and 99+ percent. Because flow data were not given, no comparison of mercury capacity or quantity of water treated can be made with the column test results of Logsdon and Symons. A 6-min empty bed contact time was recommended.

An evaluation of the results of the DWRD pilot plant study in Tables 3, 4, and 5 confirms that GAC has adsorptions capability for inorganic and organic mercury removal from tap, ground, and surface waters. In all test runs (conventional coagulation and lime softening), the cumulative mercury removal results for the virgin and exhausted GAC columns were always higher than those achieved by the conventional dual media filter. Turbidity removal was essentially the same (< 1.0 NTU) for the effluent water from all filter columns. The increase in mercury removal is therefore attributed to GAC adsorption. The pilot plant data further show that GAC is more effective for organic mercury removal than for inorganic mercury. Cumulative removals for inorganic mercury by GAC filtration ranged from 49 to 97 percent, whereas organic results ranged from 80 to near 100 percent removal. The removal data for virgin and exhausted activated carbon columns also suggest that mercury adsorption with GAC continues to occur when the GAC is exhausted for organic removal. Mercury removals by the exhausted GAC filter media were equal to or only slightly lower than those achieved by virgin activated carbon.

The ability of GAC to adsorb inorganic mercury has been demonstrated in wastewater pilot plant studies. Maruyama et al[32] conducted a pilot plant test for the removal of 0.5 mg/L of inorganic mercury from wastewater using a high lime process. The system consisted of flash mixing, flocculation, clarification, dual media filtration, and GAC filtration in series. Clarification and dual media filtration removed 70 percent of the mercury; GAC increased removals by 21 percent to a total of 91 percent.

Reverse osmosis. A review of the literature revealed several RO laboratory and pilot plant studies for the removal of metals from water or wastewater, but only the study by Johnston and Lim[25] provided data on the removal of mercury. These investigators ran a series of RO pilot plant tests to evaluate the technique for the removal of heavy metals, pesticides, and other toxic chemicals from secondary wastewater effluent. The results of one-day batch tests with spiked concentrations of 5 and 9 mg/L of inorganic mercury showed removals of 82.4 and 83.3 percent, respectively.

DWRD recently conducted two one-day tests for inorganic mercury (0.008 mg/L) removal from Glendale, Ohio, well water with two small-scale RO systems. The first system contained a spiral-wound (SW) membrane and the second a hollow fiber (HF) membrane. The SW system had a raw water flow of 2.2 L/min and operated at 1400–1600 kPa (200–230 psi) and 7–9 percent recovery. The HF system had a higher raw water flow of 5 L/min and operated at 1200–1400 kPa (170–200 psi) and 40–50 percent recovery. The test results were 25 percent removal with the SW system and 79–81 percent with the HF system.

The results of these two limited studies are not as high as the 95–98 percent rejection range for inorganic mercury estimated by equipment manufacturers.[33,34] However, full-scale RO systems operated at high pressure and recovery should achieve greater removals than pilot-scale units performing under less than optimum conditions. No data were obtained for electrodialysis removal of mercury, but this method should be as effective as reverse osmosis.

Mercury treatment summary. Conventional coagulation treatment for inorganic mercury removal is very dependent on raw water turbidity and coagulant and slightly dependent on pH. The higher the turbidity of the water, the more efficient the removal process with either alum or iron coagulants. Iron coagulation is more effective than alum, particularly when the water is low in turbidity. A slightly decreasing removal trend occurs as the pH increases from 6 to 9. Under ideal treatment conditions of high turbidity and low pH, ferric sulfate coagulant achieves only moderate removals of about 80 percent. Conventional coagulation, therefore, is only adequate for very low levels of inorganic mercury concentrations.

Conventional coagulation treatment for organic mercury removal is also very dependent on turbidity, but not on the type of coagulant. Alum and iron removals are about equal and increase as the turbidity increases. In comparison to inorganic mercury treatment, conventional coagulation is not as effective; removals are a low 20–40 percent.

Lime softening is equal to or slightly more effective than coagulation treatment for inorganic mercury and less effective for organic mercury. No organic mercury is removed, and the highest inorganic reductions of 60–70 percent take place at pH 10.5 to 11.5. Below this pH range inorganic mercury removal decreases with decreasing pH. Supplemental coagulation with ferric sulfate can increase removals by 10–15 percent.

PAC and GAC will remove inorganic and methyl mercury, but both types of activated carbon work best on the organic form of mercury. PAC will remove 20–80 percent of either form, depending on the dose and type of carbon and the pH of the treated water. To achieve a residual level of 0.002 mg/L of either inorganic or organic mercury, approximately 1 mg/L of PAC is needed for each 0.001 mg/L of Hg to be removed. PAC, therefore, may be useful to control an occasional problem from an industrial spill.

GAC performs more efficiently than PAC and is capable of higher removals of 80–100 percent with adequate contact time. Experimental data show organic mercury to be more readily removed than inorganic mercury, but this behavior is expected because activated carbon has a high capacity for organics. Insufficient data exist to predict adsorptive capacity, but the data do suggest that a 3.5–6 min contact time is necessary.

Ion exchange treatment for mercury removal has been demonstrated in the industrial wastewater field, but the method is not practical for drinking water. The type of resin required is dependent on the form of mercury, a situation over which water utilities have no control. Although expensive, reverse osmosis and electrodialysis are good methods of removing various levels and forms of mercury.

Presently, mercury is not a problem in drinking water although there are signs that the detection frequency is increasing. DWRD has no specific research projects currently (spring 1979) devoted to mercury treatment. A research grant was funded in August 1978 to the Univer-

*Filtrasorb 200, Calgon Corp., Pittsburgh, Pa.

sity of Houston to construct a mobile pilot plant containing ion exchange, activated alumina, and RO treatment units. This system will be utilized by the university to develop design and operational data at various locations in the southwest having one or more contaminants that may include mercury.

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